Studies on Catechol-functionalized Cyclosiloxane Polymers for Hybrid Nanocoating on Flexible Substrates

著者	劉 一達
number	62
学位授与機関	Tohoku University
学位授与番号	工博第5415号
URL	http://hdl.handle.net/10097/00124482

	りゅう　いーだ
氏　　　　名	劉　一　達
授　与　学　位	博士（工学）
学位授与年月日	平成２９年９月２５日
学位授与の根拠法規	学位規則第４条第１項
研究科，専攻の名称	東北大学大学院工学研究科（博士課程）応用化学専攻
学位論文題目	Studies on Catechol-functionalized Cyclosiloxane Polymers for Hybrid Nanocoating on Flexible Substrates (カテコール基を有する環状シロキサンポリマーによるフレキシブル基板上へのハイブリッドナノコーティングに関する研究)
指　導　教　員	東北大学教授　三ツ石　方也
論文審査委員	主査　東北大学教授　三ツ石方也　東北大学教授　芥川　智行　東北大学教授　長尾　大輔

論 文 内 容 要 旨

Chapter I　Introduction

The assemble techniques of semiconducting nanomaterials are important in preparing well performed optoelectronic devices because the preparation procedures are mostly based on sequential deposition of different materials. Among those bottom-up approaches, layer by layer (LbL) method is of great interest in manufacturing electronic devices, because of its strong capability in assembling thin films of different materials into one system and exerting nanometer control over film thickness. Layer materials, thin film coating methods and coated substrates are three most important factors of LbL method and cooperatively affect physicochemical properties of the assembled thin films such as the thickness, homogeneity and inter and inter layer film organization. In this thesis, a layer material used for LbL method, catechol-functionalized polysiloxane (CFPS), specifically designed for nanoparticle based flexible devices was synthesized in Chapter II. The molecular structure of CFPS (Fig. 1) was inspired by a glue protein secreted by marine mussel

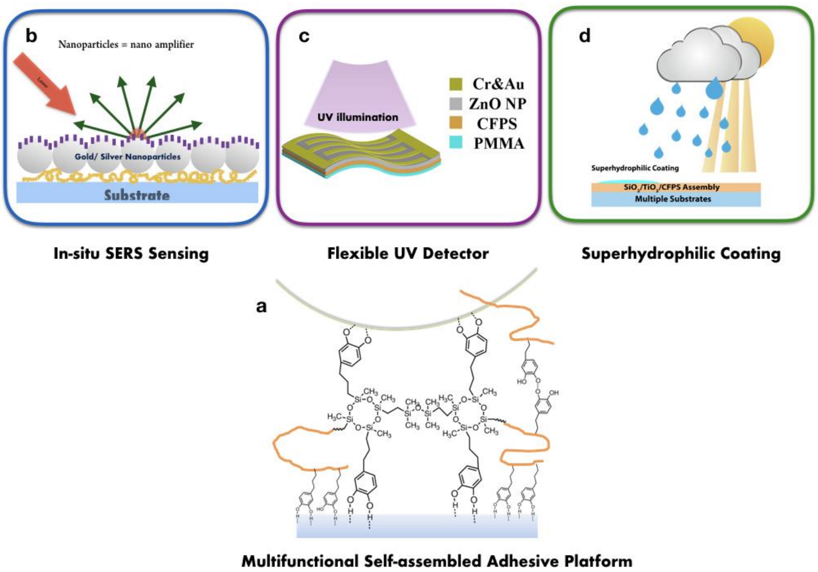

Fig.1　Catechol-functionalized polysiloxane (CFPS) for flexible nanoparticle-based device platforms.

that bond strongly to almost all organic and inorganic surfaces. The layer material is able to serve as a multifunctional platform for flexible devices because it contains the following features: 1) It induces a controllable self-assembled behavior of nanoparticles, thus manipulates device properties. 2) It will generate admirable surface robustness for a long-term durability of flexible devices, which is highly critical for true practice. 3) it has versatile compatibility for applications in different devices. Catechol can form energetic interactions with many kinds of substrates and transition metallic nanoparticles. The layer material CFPS was further applied for in-situ surface enhanced Raman scattering (SERS) sensing (Chapter III), for a long term durable ZnONP based flexible UV detector (Chapter IV) as well as for superhydrophilic surface modification on flexible polymer substrates (Chapter V). The functions of CFPS self-assembled platform were in detail studied and demonstrated in each application.

Chapter II Synthesis and Nanocoating Properties of Catechol-functionalized Polysiloxane

Eugenol, a catecholic derivative that is readily available in large quantities, was used as precursor for catechol functionalization. The first key point of the CFPS synthesis strategy is tris-(pentafluorophenyl)borane (TPFPB)-catalyzed silylation. The orthogonal reactivity of TPFPB allows the facile one-step transformation of eugenol into a reactive, bis-silyl protected DOPA mimic. The second key point of the CFPS synthesis strategy is the hydrosilylation. 1,3,5,7-Tetramethylcyclotetrasiloxane (TMCS) with four silicon hydrogen bonds and 1,3-divinyltetramethylsiloxane (DTMS) with two terminated vinyl groups were used as comonomers to form linear structure polysiloxane backbones (TMCS-DTMS polymers). Remaining silicon hydrogen bonds can further react with vinyl groups of silyl-protected eugenol through hydrosilylation for functionalization. This renders the synthesis procedure from polymerization to functionalization simply conducted in a one pot reaction. The fractional ratio of silyl-protected eugenol is 88.2% (Fig. 2), which indicates a very high concentration of catechol units introduced into the polymer backbone and will have benefits for the assembled materials with a strong adhesive property. After deprotected in mild acidic solution, CFPS was dissolved into toluene. A

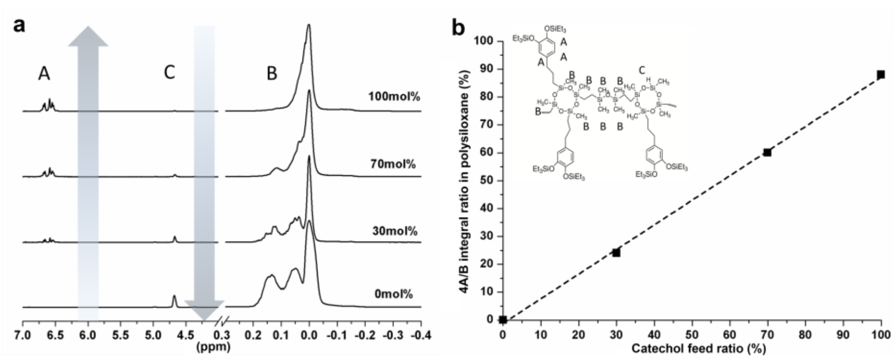

Fig. 2 Characterization of the ratio of catechol reacted with a polymer backbone. (a) ^{1}H NMR spectra of CFPS with different catechol/silicon hydrogen bond feed ratios. All spectra were normalized to the intensity of the Simethyl resonance at approximately 0 ppm. (b) Plot of the integral ratio of catechol/Si methyl (4A/B) in 1H NMR as a function of the catechol/silicon hydrogen bond feed ratio.

CFPS self-assembled thin film was prepared through dip-coating method. The CFPS self-assembled thin film has a smooth surface with a surface roughness of 4.6 nm and a thickness of 36 nm. It also has an outstanding coating ability not only on inorganic substrates such as silica wafer, glass slide and quartz but also on flexible polymers sheets such as PMMA, PET, PEN and PI. The thin film coating was also conducted onto a PMMA substrate with a nano-grating structure.

Chapter III CFPS Self-assembled Platform for In-Situ SERS Probing

Surface enhanced Raman scattering (SERS) is a physical phenomenon based on the enhancement of the magnitude of the electromagnetic fields around a roughened silver or gold metallic surface caused by localized surface plasmon resonance. It is a powerful detection method that is able to magnify the Raman signal of chemical contamination on the skin of fruits or animals even in trace amount. In this chapter, CFPS thin film assembly was introduced into silver nanoparticle (AgNP) based SERS substrates. AgNPs are anchored onto CFPS-modified substrates using a dip coating process. Scanning electron microscopy images revealed that AgNPs were distributed homogeneously on numerous substrates. Moreover, the surface number density and average interspace of the AgNPs were tuned easily by controlling the concentration of AgNP dispersions, resulting in the tunable CFPS/AgNP SERS substrate enhancement. A substrate with high-density AgNPs exhibited excellent surface enhanced Raman scattering (SERS) performance with an enhancement factor as high as 7.89×10^7 and an ultra-low detection limitation of 0.1 nM, (Fig. 3), which can be ascribed to the ‘‘hotspots’’ formed between the adjacent AgNPs controlled by CFPS-induced self-assembly. The AgNP structures prepared on different substrates using CFPS showed a similar high intensity, suggesting a versatile platform of the CFPS film for AgNP assemblies

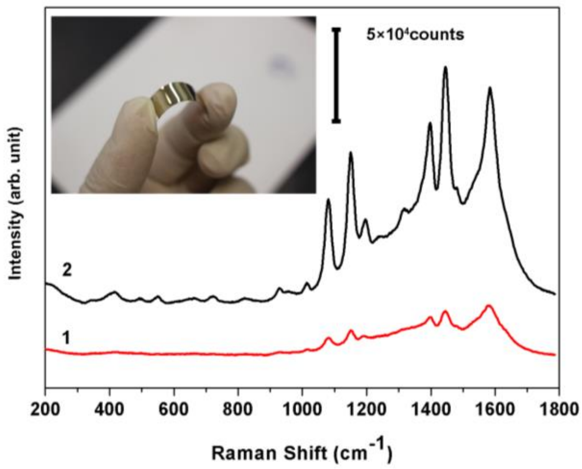

Fig. 3 SERS spectra: Line 1 and Line 2 enhancement signal using 0.1 nM and 1 mM PATP ethanol solution, respectively. (top left) PMMA-based flexible CFPS/AgNP substrate.

Chapter IV CFPS Self-assembled Platform for Flexible UV Detector

In Chapter IV, the CFPS thin film assembly was introduced into a ZnONP-based flexible UV detector to enhance the surface robustness and long-term durability of the device. The CFPS thin film assembly between flexible PMMA substrates and the semiconducting channel can strongly anchor ZnONPs through a coordination bond, thus forming an ultra-stable channel layer. A peeling test of the ZnONP channel was conducted by using a transparent 3M Scotch® tape. Laser scanned microscope proved that the semiconducting channel structure was kept integrity after the peeling test, indicating good surface robustness. The as-prepared UV detector owns a dark and optical current of 0.35 nA and 1430 nA respectively, the on/off ratio 4.03×10^3. The properties are as good as other ZnONP-based devices prepared on the solid substrate using similar preparation methods. Finally, a bending test was conducted using a home-made bending machine. The present flexible device shows a stable UV detecting performance after one thousand times of bending at 3 mm curvature radii. The CFPS adhesive self-assembly thin film provides a promising solution to increase surface stability and long term durability for all ZnONP-based optoelectronic devices.

Chapter V CFPS Self-assembled Platform for Superhydrophilic Coating

Superhydrophlicity denotes surfaces with a water contacted angle (WCA) of less than 10°, which is an inevitable feature for applications such as self-cleaning, antifogging, anticorrosive, and pervaporation. TiO_2/SiO_2 composites coating is an effective classical method generating a UV-induced superhydrophilic surface, however problems still exist: In the preparation procedure, calcination over 500 ℃ is necessary to achieve good surface robustness, which impede the application of the method to polymer surfaces. In Chapter V, the CFPS adhesive thin film assembly was introduced into the procedure of hybrid nano-coating of SiO_2NP/TiO_2NP to demonstrate superhydrophlic treatment without calcination. Catechol groups can form energetic supramolecular interactions with both SiO_2NP and TiO_2NP surfaces respectively through hydrogen bonding and coordination bonding. The strong adhesion force provided by the CFPS film allows us to further extend the method into flexible electronics without calcination process. High transparency of CFPS thin film will also maintain the transparency of light at the visible light wavelengths. After the SiO_2NP/TiO_2NP deposition with CFPS, The WCA values of PMMA, aluminum, and glass slide were 3.3°, 4.5° and 4.8° respectively. Strong surface robustness was also demonstrated by a peeling test.

Chapter VI Conclusions

In the present study, the author synthesized catechol-functionalized polysiloxane (CFPS) and further used it as a platform to induce three different self-assembled hybrid thin films (CFPS/AgNP, CFPS/ZnONP, CFPS/SiO_2NP/CFPS/TiO_2NP) for different applications as SERS substrates, flexible UV detector and superhydrophilic coating. The CFPS self-assembled thin film serves as a multifunctional platform that controls the self-assembled behavior of nanoparticles and manipulates the device properties. It will provide flexible devices with strong surface robustness, which is highly critical for practice use. The diverse compatibility also renders a huge potential of CFPS adhesive in many other nanoparticle-based flexible devices.

論文審査結果の要旨

プラスチックなど柔軟な支持基板を使用するフレキシブルエレクトロニクスは、ナノ材料の精密集積技術が重要となる。無機ナノ粒子はバルクにはみられない興味深い性質を示すが、高温での焼結処理を必要とするため耐熱性に乏しいプラスチック基板上への集積は困難である。本論文は、カテコール基を有する環状シロキサンポリマー（CFPS）を用い、様々なナノ粒子と組み合わせたボトムアップ的ハイブリッドナノコーティングをプラスチック基板上で検討した研究の成果をまとめたものであり、全編6章より構成されている。

第1章は緒言であり，本研究の背景と目的について述べている。

第2章では四官能性環状シロキサンをビルディングブロックとして二官能性シロキサンコモノマーとのヒドロシリル化反応により直鎖型環状シロキサンポリマーを合成した。シリル基で保護されたeugenolと環状シロキサンポリマーとのヒドロシリル化反応について、置換率88%と高効率でカテコール基を導入できることを明らかにした。得られたCFPSのトルエン溶液を用い、基板を溶液に浸漬するディップ法により、シリコンウェハやガラス基板、さらにはPMMAとPET、PIなどのプラスチック基板上に均一ナノコーティングが約40 nmの膜厚で可能であることを実証した。

第3章では、銀ナノ粒子およびフレキシブル基板との接着層としてCFPSを応用している。市販の銀ナノ粒子水溶液の濃度に応じ、CFPS 表面に固定される銀ナノ粒子の表面密度制御および高密度均一コーティングが可能であること、さらに銀ナノ粒子がCFPS表面に非常に強固に固定されていることを剥離試験により明らかにしている。銀ナノ粒子とCFPSのハイブリッドナノコーティングをラマン散乱センサーとして検討したところ、10^7のシグナル増強度が得られ、0.1nMの検出感度を有することを明らかにしている。さらに、フレキシブル性を生かして果物表面での同時測定を実証し、180□までの耐熱性を有していることを明らかにするなどこれまでに見られないフレキシブル表面増強ラマンセンサーの構築に成功している。

第4章では、ZnOナノ粒子とCFPSのハイブリッドコーティングをとおし、光電変換に基づくフレキシブル紫外光検出センサーについて検討している。PMMA基板上にディップコーティングしたCFPSをテンプレートとして ZnO ナノ粒子をスピンコーティングし金電極を蒸着することでセンサーを作製した。50から700 μWcm^{-2}領域で7.77×10^{-2} A/Wの応答性を示し、1000回の曲げ試験にも耐えられるフレキシブル紫外光検出センサーとして機能することを明らかにしている。

第5章では、CFPSをバインダーとしてSiO_2ナノ粒子とTiO_2ナノ粒子の精密集積を行っている。ガラス、PMMA、アルミ箔の三種類の基板上にCFPS、SiO_2ナノ粒子、CFPS、TiO_2ナノ粒子の順で精密集積を行い、紫外光照射することで水の接触角5°以下の超親水性表面を構築した。CFPSがSiO_2ナノ粒子とTiO_2ナノ粒子の両者を強固に基板上に固定できる結果、高温での焼結処理を施すことなく、フレキシブル基板上に透明で(透過率70%)、長期間安定な超撥水表面の構築に成功している。

第6章は本論文の総括である。

以上要するに本論文は，環状シロキサンの多官能性に着目し、環状シロキサンポリマーの高分子化と得られるポリマーの高効率機能化を利用した機能性環状シロキサンポリマーの創製を実証した。環状シロキサンポリマーがもつ柔軟性とカテコール基による修飾化がもたらす接着多様性を利用して、フレキシブルエレクトロニクスに重要なハイブリッドナノ集積技術の要素材料として展開し、シロキサンポリマーの機能化による応用展開の可能性、および作製工程の簡素化への方法論を明示した。得られた研究成果は高分子化学及び材料化学の発展に寄与するところが少なくない。

よって、本論文は博士(工学)の学位論文として合格と認める。